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Synthesis and electrochemical characterization of stoichiometric Cu_2S as cathode material with high rate capability for rechargeable lithium batteries

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HIGHLIGHTS

- Stoichiometric Cu_2S was prepared by spray pyrolysis followed by heat treatment.
- Electrochemical reaction of Cu_2S was studied by exsitu X-ray diffraction analysis.
- Monoclinic Cu_2S was formed into tetragonal $Cu_{1.96}S$ during initial five cycling.
- Cu_2S coated on Al foil leads to serious capacity fading owing to Al corrosion by Cu.
- Cu_2S coated on Cu foil demonstrated stable cyclability at high rate of up to 30 C.

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ABSTRACT

Synthesis of stoichiometric copper sulfide (Cu_2S) was studied by spray pyrolysis (SP) with heat treatment for different Cu/S molar ratios in the starting solution and different synthesis and annealing temperatures. The sample prepared via SP at 400 °C and then annealed at 460 °C for 2 h showed the stoichiometric Cu/S ratio, which was verified by inductively coupled plasma-optical emission spectroscopy. The X-ray diffraction (XRD) peaks of the sample were indexed to the monoclinic structure with space group $P2_1/c$. The electrochemical performance of the stoichiometric Cu_2S electrode was investigated by a cycle test and differential capacity analysis. The Cu_2S electrode coated on an Al foil exhibited a first discharge capacity of 335 mAh g^{-1} at a charge-discharge rate of 0.1 C, which corresponds to 99.4% of its theoretical capacity. However it showed poor reversibility owing to the corrosion of Al foil by Cu. In contrast, the Cu_2S electrode coated on Cu foil demonstrated stable cyclability at high charge-discharge rates of up to 30 C. Exsitu XRD analysis showed that a phase transformation from the monoclinic Cu_2S structure with the space group $P2_1/c$ to the tetragonal $Cu_{1.96}S$ structure with the space group $P4_32_12$ gradually progressed during the initial five cycles.

1. Introduction

Among the many competing technologies for energy storage, lithium-ion batteries (LIBs) are the most important technology and have been used in various applications such as electric vehicles (EVs), portable electronics devices, and memory backup systems. Current LIBs mainly consist of an intercalation-based graphite anode coupled with a lithium-transition-metal oxide or phosphate cathode. However, owing to their limitations in terms of energy density, cost, and safety, current LIBs are unable to power EVs and smart grids. These issues have led to a search for alternative electrodes, and conversion-based metal sulfides [1] and fluorides [2] have been found to exhibit higher capacities than the traditional insertion-based metal oxide electrodes ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, etc.) [3].

In the copper sulfide family (Cu_xS), Cu_2S is attracting interest as a promising conversion-based cathode material for rechargeable

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lithium batteries owing to its high theoretical capacity (337 mAh g^{-1}) and energy density (553 Wh kg^{-1}), and good electronic conductivity (10^{-4} S cm^{-1}). Recently, it is also expected to use as cathode materials for all solid state lithium sulfur batteries. However, Cu_2S suffers from poor capacity retention and therefore has a short lifetime [4].

Thus far, various synthesis methods such as the general solution method [1], atomic layer deposition [5], dry thermal sulfuration [6], the non-hydrolytic sol-gel method [7], the hydrothermal method [8–10], and spray pyrolysis (SP) [11,12] have been reported as means of preparing Cu_2S thin films and particles. However, a synthesis route for stoichiometric Cu_2S with the monoclinic structure has not been established. Furthermore, several electrochemical reaction mechanisms for Cu_2S electrodes have been investigated by exsitu X-ray diffraction (XRD) analysis [4,13–15]. However, the chemical composition of the as-prepared or commercial samples used in the electrochemical testing was not verified as a stoichiometric Cu_2S by any characterizations in their studies. As a result, few investigations on the electrochemical reaction mechanism of stoichiometric Cu_2S with the monoclinic structure have been carried out, despite the electrochemical properties of Cu_xS being strongly affected by their chemical composition [13].

In this work, we prepared stoichiometric Cu_2S with the monoclinic crystal structure, which was verified by XRD and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses, via SP followed by heat treatment. In order to determine the reason for its poor capacity retention, the electrochemical properties of stoichiometric Cu_2S electrodes coated on Al foil, carbon paper and Cu foil current collectors were also investigated in conjugation with exsitu XRD analysis.

2. Experimental

2.1. Precursor solution

The precursor solution was prepared by dissolving accurately measured amounts of copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) and thiourea ($CS(NH_2)_2$) in distilled water, in which the Cu/S molar ratio was varied from $[Cu/S]_0 = 0.5$ to 2.0 with a fixed copper concentration ($[Cu]_0 = 0.05$ mol L^{-1}). All chemicals were purchased from Wako Pure Chemical Industries Ltd.

The thermal decomposition of $Cu(NO_3)_2 \cdot 3H_2O$ was determined using Rigaku Thermo Plus 8120 thermogravimetry (TG)-differential thermal analysis (DTA) apparatus under a heating rate of 5 °C min^{-1}, an atmosphere of dry He, and a flow rate of 150 ml min^{-1}.

2.2. Synthesis of stoichiometric Cu_2S

A schematic diagram of the experimental apparatus has been described elsewhere [16]. It consists of an ultrasonic nebulizer (1.7 MHz, Omron Co., Ltd., Model NE-U12), a laminar flow aerosol reactor (a high-quality ceramic tube of 20 mm inner diameter and 1.50 m length), and an electrostatic precipitator. The precursor solution was atomized at a frequency of 1.7 MHz using the ultrasonic nebulizer. The sprayed droplets were carried to the reactor, heated by an electric furnace in a 3% H_2+N_2 atmosphere, and converted into solid particles through the evaporation of the solvent, the precipitation of the solute, drying, and pyrolysis within the laminar flow aerosol reactor. The resulting particles were collected at the reactor exit by the electrostatic precipitator at 150 °C, while the gases were dried and cleaned by passing them through a cold trap. The flow rate of the gas was fixed at 2 L min^{-1} and the reactor temperature was varied from 400 to 700 °C. As-prepared samples were annealed in the temperature range from 400 to 600 °C in a 3% H_2+N_2 atmosphere for 2 h.

2.3. Sample characterization

Samples were characterized by XRD (Ultima IV with D/tex Ultra, Rigaku) with Cu-Kα radiation for crystalline phase identification. The lattice parameters of the samples were determined by Rietveld refinement of the XRD data using PDXL (Rigaku, Ver. 1.3.0.0) software. ICP-OES (Shimadzu, ICPS-7510) was used to verify the Cu/S molar ratio in the prepared samples. The morphology of the Cu_2S samples was examined by field-emission scanning electron microscopy (FE-SEM, Hitachi, S4500). The measurements and the calculation of the particle size distribution, geometric mean diameter, $d_{p,g}$, and geometric standard deviation, σ_g, have been described elsewhere [17].

The specific surface area of the sample was determined by the Brunauer-Emmett-Teller (BET) method from N_2 absorption-desorption isotherms. The N_2 adsorption–desorption measurements were performed at a liquid N_2 temperature of 77 K using a Micromeritics TriStar II 3020 system.

2.4. Fabrication of electrochemical cells and electrochemical measurements

The electrochemical properties of the stoichiometric Cu_2S were investigated using a CR2032 coin cell. The cell comprised a lithium metal electrode and a Cu_2S positive electrode separated by a microporous polypropylene separator. A 1 M lithium bis(trifluoromethane sulfonamide) (LiTFSI) in 1,3-dioxolane (DOL) and dimethoxyethane (DME) with a volume ratio of 1:1 (Tomiyama Pure Chemical Co., Ltd.) was used as an electrolyte. The Cu_2S positive electrode consisted of 80 wt% Cu_2S, 10 wt% polyvinylidene fluoride (PVDF) as a binder, and 10 wt% acetylene black (AB) as a conducting agent. These materials were dispersed in 1-methyl-2-pyrrolidinone (NMP), and the resultant slurry was then spread onto an Al foil, a carbon paper (Toray Paper TGP-H-030 5% Wet Proofing) or a Cu foil current collector using the doctor blade technique. The coated sheet was dried for 4 h in a vacuum oven set at 60 °C and then pressed to achieve good adherence between the coated material and the current collectors. The electrode was formed by punching a circular disc from the coated sheet and scraping it to standardize the area of the cathode (100 mm^2). The coin cell was assembled inside a glove box filled with high-purity argon gas (99.9995% purity). Electrochemical measurements were conducted at room temperature using a multichannel battery test system (HJ1010mSM8A, Hokuto Denko). Cells were cycled galvanostatically in the potential range between 1.0 and 3.0 V at various charge-discharge rates ranging from 0.1 to 30 C (1 C = 337 mA g^{-1}). Differential capacities (dQ/dV) were calculated from the charge and discharge profiles of an arbitrary cycle, which were measured at 0.1C using a 580 Battery Test System (Scribner Associates Inc.), using BCycle and BView software (Scribner Associates Inc.). Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron 1255B frequency response analyzer connected to a Solartron SI 1287 electrochemical interface. The amplitude of the ac signal was 10 mV in the frequency range from 100 kHz to 0.01 Hz.

To investigate the change in the structure of the stoichiometric Cu_2S positive electrodes during the discharge and charge processes, exsitu XRD analysis was conducted on the Cu_2S positive electrodes recovered from the cells after the desired number of cycles. Before this analysis, the recovered electrodes were washed with DOL, then dried at 60 °C for 2 h in an argon-filled glove box, and finally sealed with a Kapton® film to prevent exposure to air.